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DYNAMICS OF THE CHEMISTRY OF ELECTRONICALLY EXCITED ATOMS IN DE--ETC(U)
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Final Report

DYNAMICS OF THE CHEMISTRY OF ELECTRONICALLY EXCITED ATOMS
IN DEFINED QUANTUM STATES.

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I. INTRODUCTION

In its original conception, the research proposed in 1975 to the Office of Naval Research was concerned with a study of the chemical kinetics of electronically excited atoms in defined quantum states. Two major questions had to be addressed. Firstly, sources of electronically excited atoms had to be developed and quantified. During the course of this investigation these excited species were produced by photodissociation of small molecules. Hence a substantial fraction of our research effort was directed toward establishing the quantum efficiencies for production of electronically excited species by photolysis. This information was also of significance because it could be utilized in the modeling of photo-initiated chemical lasers.

Having generated the electronically excited atoms under study we would then be concerned with understanding their fate upon bimolecular collisions with other atoms and molecules. While much information was available on the overall deactivation efficiency of a variety of electronically excited states, relatively little was known in 1975 about the product species formed during these collisional encounters. A primary goal of our research was the measurement, not only of total deactivation cross-sections, but also the relative branching ratios for chemical reaction vs chemical quenching to the ground electronic state. Furthermore studies were designed to enable us to determine whether electronic orbital angular momentum would be conserved in reactive collisions. This question was of some significance in designing new chemical lasers derived from efficient sources of electronically excited species.

Finally, these studies provided the necessary information to

reconcile earlier work carried out under single-collision conditions with those obtained in "bulk" experiments. The experimental program described in the following section led to a more complete understanding of the chemical kinetics of electronically excited atoms, provided useful information for modeling of available laser systems, and suggested new routes for the construction of entirely novel chemical lasers. The research carried out under the sponsorship of the Office of Naval Research has permitted a remarkable fusion of fundamental molecular physics with practical laser technology and illustrates the synergistic roles of fundamental research and technical advancement.

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II. SUMMARY OF RESEARCH ACTIVITIES

It is often the case that development in a scientific field depends critically upon the refinement of experimental techniques and methods. In the research funded by the Office of Naval Research, several new techniques were developed in this laboratory in order to study the chemical kinetics of atoms in defined quantum states. In particular, the method of time-resolved atomic absorption spectroscopy was made quantitative through the use of high speed digital acquisition and signal averaging apparatus, in conjunction with interfaced calculators and computers. When this research was begun only rudimentary data analysis capabilities were available. By the time the contract was over, highly sophisticated numerical analysis packages were available to extract meaningful detailed kinetic information from even the weakest signals. Excitation of specific atomic states, first accomplished by white-light photolysis of suitable source molecules, was uniformly displaced by the use of lasers. This permitted high selectivity as well as good pumping efficiency. The advent of tunable dye lasers resulted in the development of Laser Induced Photodissociation Spectroscopy (LIPS) with which the atomic states of a specific photodissociation process could be observed. This, in turn, led to the elucidation of the individual contributions of specific molecular transitions to the continuum absorption in small molecules. Finally, a technique was developed for measuring weak continuous absorption spectra underlying strong banded regions of absorption. This method, known as Band Avoidance Continuum Absorption Spectroscopy (BACAS), was crucial to studies of the excited state potential curves for homonuclear diatomic molecules.

The techniques outlined above have been applied to a variety of problems in chemical kinetics. The scientific aspects of these research activities are outlined below with reference being made to the publications derived from this research program as listed in appendix A.

A. Photolysis of Alkyl Halides

The photolysis of alkyl bromides and iodides has been shown to result in the efficient production of electronically excited halogen atoms, $\text{Br}(^2\text{P}_{1/2})$ and $\text{I}(^2\text{P}_{1/2})$. Such photolytic processes have been exploited to produce an inversion between the populations of the excited state and the ground $^2\text{P}_{3/2}$ state with consequent laser action. In the early stages of this experimental program, we set out to examine the photodissociation of such molecules because of their importance in chemical laser systems. The yield of electronically excited iodine atoms, $\text{I}(^2\text{P}_{1/2})$, following the flash photolysis of alkyl iodides was found to be a strong function of the alkyl group structure (1-4). Alkyl iodides possessing secondary or tertiary α -carbon atoms displayed the lowest yields of electronically excited atoms. The relative yield of excited iodine was shown to be correlated with the ionization potential of the alkyl group. We were able to demonstrate (3) that the observed results could be explained in terms of weakened spin-orbit coupling in molecules with branched alkyl groups. This led to mixing of the alkyl iodide excited states which, in turn, resulted in low yields of electronically excited atoms. The known high yields observed for the fluorinated species was thus ascribed to the high ionization potentials of the alkyl groups.

A similar study on the alkyl bromides demonstrated that the yield of electronically excited bromine atoms resulting from the photodissociation of alkyl bromides was significantly lower than that of excited iodine atoms from the photolysis of alkyl iodides (9). In addition, the alkyl bromides were significantly more efficient in collisionally deactivating excited bromine atoms than was the corresponding deactivation for the iodides. Only CF_3Br and $\text{C}_2\text{F}_5\text{Br}$ were found to be suitable sources for production of a population inversion in bromine.

An additional study was concerned with determining the deactivation efficiencies of $\text{I}(^2\text{P}_{1/2})$ by the alkyl iodides and photolysis products. It was possible to demonstrate that the excited iodine atoms were, in fact, deactivated upon collision with alkyl radicals and hydrogen atoms as well. The rate constants derived in this way were, at the time, unique and contributed significantly to the modeling of the photochemical iodine laser system. In addition, the collisional quenching of $\text{I}(^2\text{P}_{1/2})$ by H atoms were shown to be efficient. This was, by itself, a significant observation which suggested that such processes must occur by efficient curve crossings in the HI molecule resulting from such collisions.

B. Photodissociation of Halogens and Pseudohalogens.

The absorption spectra and electronic structure of halogen molecules have been widely studied and classical investigations have permitted the precise characterization of the potential curves of both the ground and excited states in bound regions. Repulsive states, as well as portions of bound excited states lying above the dissociation threshold, have not been well characterized, however,

because classical methods cannot be applied to their study. Using LIPS we were able to deconvolute the continuous absorption spectrum of Br_2 in the visible region below 500 nm (8,11). This was accomplished by monitoring the attenuation of the atomic resonance line $5^2\text{P}_{3/2} \rightarrow 4^2\text{P}_{3/2}$ in the vacuum ultraviolet following tunable laser photodissociation of molecular bromine. By application of the reflection principle it was possible to estimate the shape of the potential curve associated with the $^3\Pi_{0+u}$ and $^1\Pi_{1u}$ states with considerable precision. The results obtained in this study suggested that earlier theoretical treatments purporting to account for the temperature dependence of the continuum absorption spectrum were, in fact, incorrect, but that results obtained by magnetic circular dichroism were in excellent accord with our direct measurements.

Not so easy to characterize was the weak absorption due to transitions from the ground state to the $^3\Pi_{1u}$ state. By inserting a cell containing molecular bromine into the cavity of a tunable dye laser it was possible to quench oscillation of the laser on the discrete lines associated with transitions from the ground state to the $^3\Pi_{0+u}$ state. This yielded a light source which effectively only probed the weak continuum absorption (13). These studies yielded a continuum absorption profile which was in excellent agreement with the single point derived from earlier studies using a frequency doubled Nd laser and represented the first use of an intracavity absorption technique for measuring quantitatively a weak absorption signal in the presence of strong banded spectra.

White light photolysis of ICN in the continuum region near 260 nm was shown (14) to produce electronically excited iodine atoms with a quantum yield of 0.5 ± 0.1 . This was in good accord with

earlier studies using photofragment spectroscopy and laser induced fluorescence. An efficient deactivation of $I(^2P_{1/2})$ by CN radicals was shown to occur. We hope to measure the quantum yield of electronically excited iodine atoms following the photodissociation of ICN as a function of wavelength in the middle ultraviolet in order to further elucidate the electronic structure of this molecule in its low-lying excited states.

C. The Role of Chemical Reaction in the Collisional Deactivation of Electronically Excited Halogen Atoms.

One of the most important aspects of this research program was the elucidation of the mechanism by which electronically excited halogen atoms were deactivated. A variety of collision partners were studied and both energy transfer and chemical reaction were seen to play an important role.

The collisional deactivation of electronically excited bromine atoms, $Br(^2P_{1/2})$, upon collision with hydrogen, deuterium and HD was studied by monitoring the temporal profile of the excited atom concentration by atomic absorption spectroscopy in the vacuum ultraviolet (6). Relatively efficient electronic to vibrational energy transfer was inferred from this study. The experimental results were compared to theoretical predictions. While the latter were in qualitative agreement with the experimental results, it appears that they significantly underestimated non-resonant processes in the deactivation of electronically excited bromine by the hydrogen isotopes.

Collisional deactivation of electronically excited iodine atoms, $I(^2P_{1/2})$, by chemical reaction with HBr and DBr was also

studied. By monitoring the growth of ground state iodine atoms following deactivation it was possible to estimate the efficiency of chemical reaction vs physical quenching to the ground state, $^2P_{3/2}$. Our experimental results demonstrated quite clearly that both for HBr and DBr, chemical reaction played a dominant role. This was the first demonstration of an efficient non-adiabatic reaction in excited state deactivation of the halogens and suggested that virtual states correlating with vibrationally excited molecular reactants might play an important role in fixing the overall efficiency by which electronically excited atoms are quenched.

The studies on deactivation of excited iodine atoms by HBr were closely followed by further studies of the deactivation of $I(^2P_{1/2})$ by Br_2 (10,11). These experiments not only involved monitoring the production of ground state iodine atoms but also, by the use of atomic absorption spectroscopy, permitted observation of both ground and electronically excited state bromine atoms. The deactivation of electronically excited iodine was shown to proceed to a large degree via chemical reaction, the predominant product being $Br(^2P_{1/2})$. The quantitative results suggested that a bromine atom chemical laser based on the reaction of electronically excited iodine atoms with Br_2 would be feasible. Subsequent work in the laboratory of C. Wittig demonstrated laser action on the bromine atom transition. This represents an almost unique example of electronic angular momentum conservation leading to chemical laser action involving low-lying excited states and represents a major accomplishment of this research program. A simple molecular orbital model of the reaction of iodine atoms with molecular bromine predicted that this efficient chemical interaction would proceed

by way of a side-on approach of the halogen atom to the molecule and suggested new theoretical methods for the analysis of such chemically interesting processes.

D. Energy Storage in Electronically Excited Alkaline Earth Atoms.

The storage of energy in electronically excited alkaline earth atoms is of particular interest because of the high efficiency with which such states may be produced using an electric discharge. Using high intensity tunable radiation, it was possible to populate both the optically metastable excited state of barium, $\text{Ba}(^3\text{D}_J)$, and calcium, $\text{Ca}(^3\text{P}_J)$ (15,16). The cross-section at 730 K for deactivation of electronically excited barium by ground state barium atoms was large, 1.3 nm^2 . This was in good agreement with theoretical calculations of molecular bonding in the group IIA dimers which suggested that the lowest-lying state of Ba_2 correlates with $\text{Ba}(^3\text{D}_J)$. This state crosses the potential curve correlating with two ground state barium atoms at large (0.5 nm) internuclear distances suggesting the possibility of an efficient curve crossing resulting in a large cross-section for collisional deactivation of the metastable barium atoms.

Deactivation of $\text{Ca}(^3\text{P}_J)$ by calcium atoms in the ground electronic state is slow. This again is in accord with theoretical calculations which show that no low-lying electronic state of Ca_2 which correlates with $\text{Ca}(^3\text{P}_J)$ is sufficiently strongly bound to cross the potential curve correlating with two ground state calcium atoms. Electronically excited calcium is, however, deactivated quite efficiently ($\sigma = 0.26 \text{ nm}^2$ at 850 K) by barium atoms. This, in turn, suggests that such crossings do indeed occur in the alkaline earth dimer CaBa . We were disappointed not to be able to observe production

of any of the energetically accessible electronically excited states of barium which could result following energy transfer from electronically excited calcium to ground state barium. Such studies will require more sensitive measurements involving laser induced fluorescence. Clearly, techniques are now available to enhance our detailed understanding of the dynamics of collisions involving electronically excited atoms in the gas phase.

Appendix A

Publications Supported by this Contract

1. "Direct Determination of the Yield of Electronically Excited Iodine Atoms, $I(5^2P_{1/2})$, in the Flash Photolysis of Alkyl Iodides", T. Donohue and J. R. Wiesenfeld, I.E.E.E. J. Quant. Elec., QE-11, 705 (1975).
2. "Relative Yields of Electronically Excited Iodine Atoms, $I(5^2P_{1/2})$, in the Photolysis of Alkyl Iodides", T. Donohue and J. R. Wiesenfeld, Chem. Phys. Lett., 33, 176 (1975).
3. "Photodissociation of Alkyl Iodides", T. Donohue and J. R. Wiesenfeld, J. Chem. Phys., 63, 3130 (1975).
4. "Molecular Aspects of Photochemical Dissociations", J. R. Wiesenfeld in "Spectroscopy of the Excited State", B. Di Bartolo, Ed., Plenum Press, New York, 1975, p. 385.
5. "Photochemistry of Alkyl Iodides", T. Donohue and J. R. Wiesenfeld, J. Phys. Chem., 80, 437 (1976).
6. "Collisional Deactivation of $Br(4^2P_{1/2})$ by Hydrogen Isotopes", J. R. Wiesenfeld and G. L. Wolk, J. Chem. Phys., 65, 1506 (1976).
7. "Deactivation of $I(5^2P_{1/2})$ by Chemical Reaction with HBr and DBr", J. R. Wiesenfeld and G. L. Wolk, J. Chem. Phys., 67, 509 (1977).
8. "Laser Induced Photodissociation Spectroscopy: Br_2 ", T. G. Lindeman and J. R. Wiesenfeld, Chem. Phys. Lett., 50, 364 (1977).
9. "Photodissociation of Alkyl Bromides", W. L. Ebenstein, J. R. Wiesenfeld and G. L. Wolk, Chem. Phys. Lett., 53, 185 (1978).
10. "Dynamics of the Deactivation of $I(5^2P_{1/2})$ by Br_2 . I. Quenching of Excited Iodine Atoms", J. R. Wiesenfeld and G. L. Wolk, J. Chem. Phys., 69, 1797 (1978).

11. "Dynamics of the Deactivation of $I(5^2P_{1/2})$ by Br_2 . II. Production of Electronically Excited Bromine Atoms, $Br(4^2P_{1/2})$, by Chemical Reaction", J. R. Wiesenfeld and G. L. Wolk, J. Chem. Phys., 69, 1805 (1978).
12. "Photodissociation of Br_2 in the Visible Continuum", T. G. Lindeman and J. R. Wiesenfeld, J. Chem. Phys., 70, 2882 (1979).
13. "Measurement of the $A^3\Pi_{1u} \leftarrow X^1\Sigma_g^+$ Continuum Absorptivity in Br_2 ", C. P. Hemenway, T. G. Lindeman, and J. R. Wiesenfeld, J. Chem. Phys., 70, 3560 (1979).
14. "Efficient Production of $I(5^2P_{1/2})$ in the Photodissociation of ICN", S. T. Amimoto, J. R. Wiesenfeld, and R. H. Young, Chem. Phys. Lett., 65, 402 (1979).
15. "Quenching of Electronically Excited Barium Atoms", P. G. Whitkop and J. R. Wiesenfeld, J. Chem. Phys., 72, 1297 (1980).
16. "Collisional Deactivation of $Ca(4p^3P_J)$ by Barium Atoms", P. G. Whitkop and J. R. Wiesenfeld, Chem. Phys. Lett., 69, 457 (1980).

Appendix B

Ph.D. Theses Supported by this Contract

1. G. L. Wolk - Reactive and Physical Deactivation of Electronically Excited Bromine and Iodine Atoms (1978)
2. T. G. Lindeman - Laser Spectroscopic Studies of Bromine (1979)
3. R. H. Young - Photodissociation of Small Molecules (1981)